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Kinetics of Ce and Nd scavenging in Black Sea waters

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Abstract

Mixing experiments were performed during Leg 5 of the 1988 Black Sea Expedition in order to learn more about the mechanism and kinetics of rare earth element (REE) scavenging at the oxic–anoxic interface of anoxic basins and, more specifically, in the suboxic zone of the Black Sea. Water from the depth of the dissolved REE maxima (300 dbar) was mixed in a thermostated reaction vessel with water from the depth of the particle maximum (PM) that had previously been equilibrated with the atmosphere. Subsamples were taken from the reaction vessel over a period of 24 h and analyzed for dissolved Ce (a redox reactive REE) and Nd (a non-redox reactive REE). During the first 2.5 h both Ce and Nd were removed from solution at a high rate, presumably as a result of adsorption onto fresh Mn and/or Fe oxides that formed during equilibration of the PM end-member with the atmosphere. The rates of Ce and Nd removal were approximately the same, suggesting that oxidative scavenging of Ce was of minor importance. After 2.5 h both Ce and Nd were released again at a rate much lower than that of the initial removal, presumably as a result of reductive dissolution of the Mn and/or Fe oxides onto which they were adsorbed. While this reductive dissolution may have been caused by sulfide that was introduced with the 300 dbar end-member, the results of a separate mixing experiment in the presence of a bio-inhibitor (formaldehyde) suggest that Mn and Fe reducing bacteria also played a significant role. The initial removal as well as the subsequent release of Ce and Nd were found to obey pseudo first-order kinetics.

1. Introduction

The discovery of a broad suboxic zone overlying the anoxic water in the Black Sea was certainly the most exciting result of the 1988 Black Sea Expedition. The oxic-anoxic interface had undergone radical changes since previous US cruises in 1969 (R/V *Atlantis II*) and 1975 (R/V *Chain*). Near the centre of the western gyre the first appearance of sulfide in the watercolumn had risen by as much as 30 m and was overlain by a 10–40 m thick layer within which oxygen concentrations did not exceed 5 μM (Murray and Izdar, 1989; Murray et al., 1989). In general, the suboxic zone was broader towards the centre of the gyre; at near-shore stations it was much less discernable and sometimes completely absent (Tebo, 1991).

Vertical distributions of dissolved and particulate Fe and Mn at a station in the centre of the Black Sea (Fig. 1) were reported by Lewis

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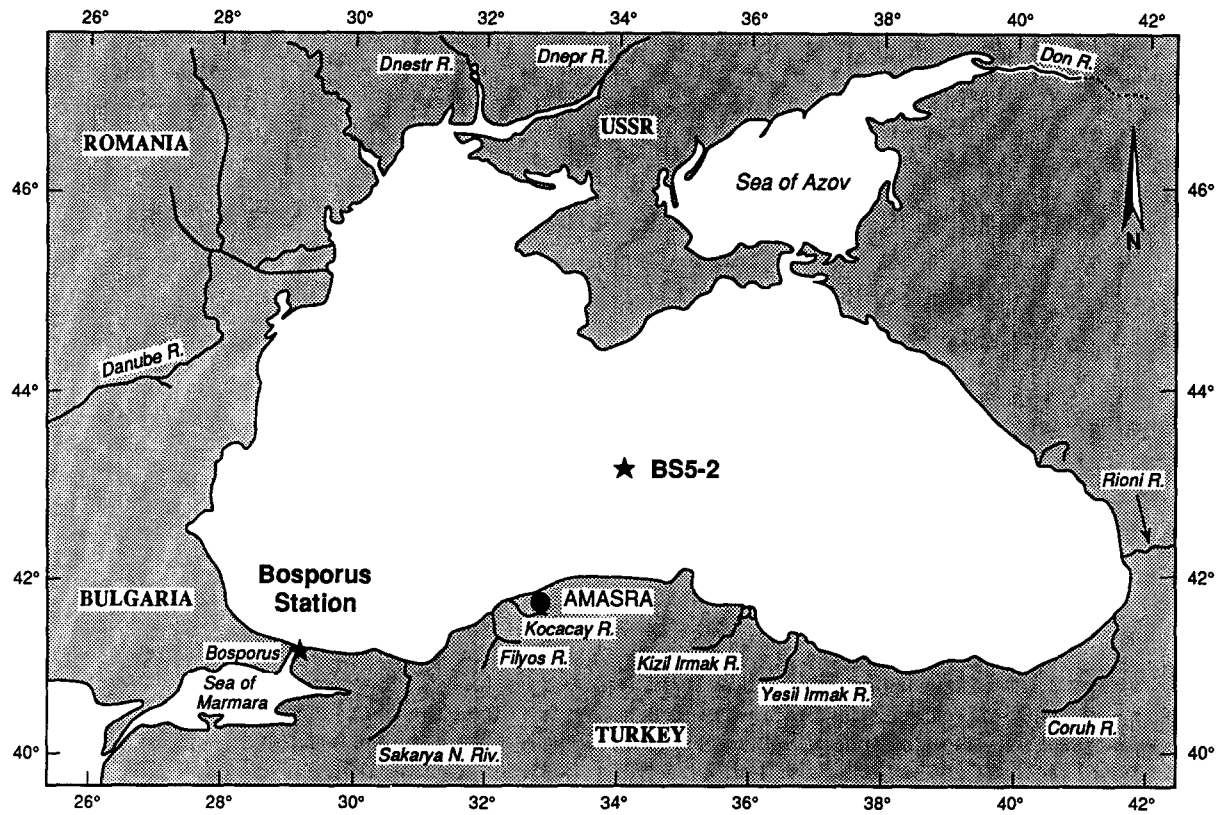


Fig. 1. Map of the Black Sea. Mixing experiments were performed at station BS5-2 (43°06′N, 34°00′E), which was occupied during Leg 5 of the 1988 Black Sea Expedition.

and Landing (1991) and by Landing and Lewis (1991). Mn oxidation was studied at the same station by Tebo (1991). Fe cycling seemed to take place near the bottom of the suboxic zone, as signified by the onset of the dissolved Fe gradient. Mn cycling seemed to take place near the top of the suboxic zone, where the onset of the dissolved Mn gradient roughly coincided with a distinct particulate Mn maximum. Surprisingly, a second particulate Mn maximum was observed near the bottom of the suboxic zone, where there was apparently no oxygen to sustain Mn oxidation (Fig. 2a). There has been considerable debate as to the origin of the lower particulate Mn maximum, which coincided with a light transmission minimum, indicative of a dense layer of particles, and possibly also with a total bacteriochlorophyll-e maximum (Fig. 2b). Tebo (1991) found it to be associated with very high rates of microbially mediated Mn oxidation and suggested that this Mn oxidation is sustained by a lateral flux of oxygen from the southwestern shelf or, alternatively, that Mn is oxidized at the southwestern shelf and then laterally transported to the centre of the Black Sea.

Schijf et al. (1991) reported that the onset of dissolved REE gradients at station BS5-2 (Fig. 1) coincided with the onset of the dissolved Fe gradient near the bottom of the suboxic zone. In addition, Schijf (1992) reported that the onset of dissolved REE gradients coincided with single particulate REE maxima at the depth of the lower particulate Mn maximum (Fig. 2c). Schijf et al. (1991) concluded that REE cycling in the Black Sea is related to Fe cycling and apparently decoupled from Mn cycling. This was disputed, however, by German et al. (1991) whose data suggest that REE cycling takes place at the same depth as Mn cycling. Sholkovitz (1992) recently commented that neither conclusion can be drawn

on the basis of the available data. German et al. (1992) attributed the discrepancy to the dynamic nature of the watercolumn at station BS5-2, which was located at the boundary between the two main Black Sea gyres.

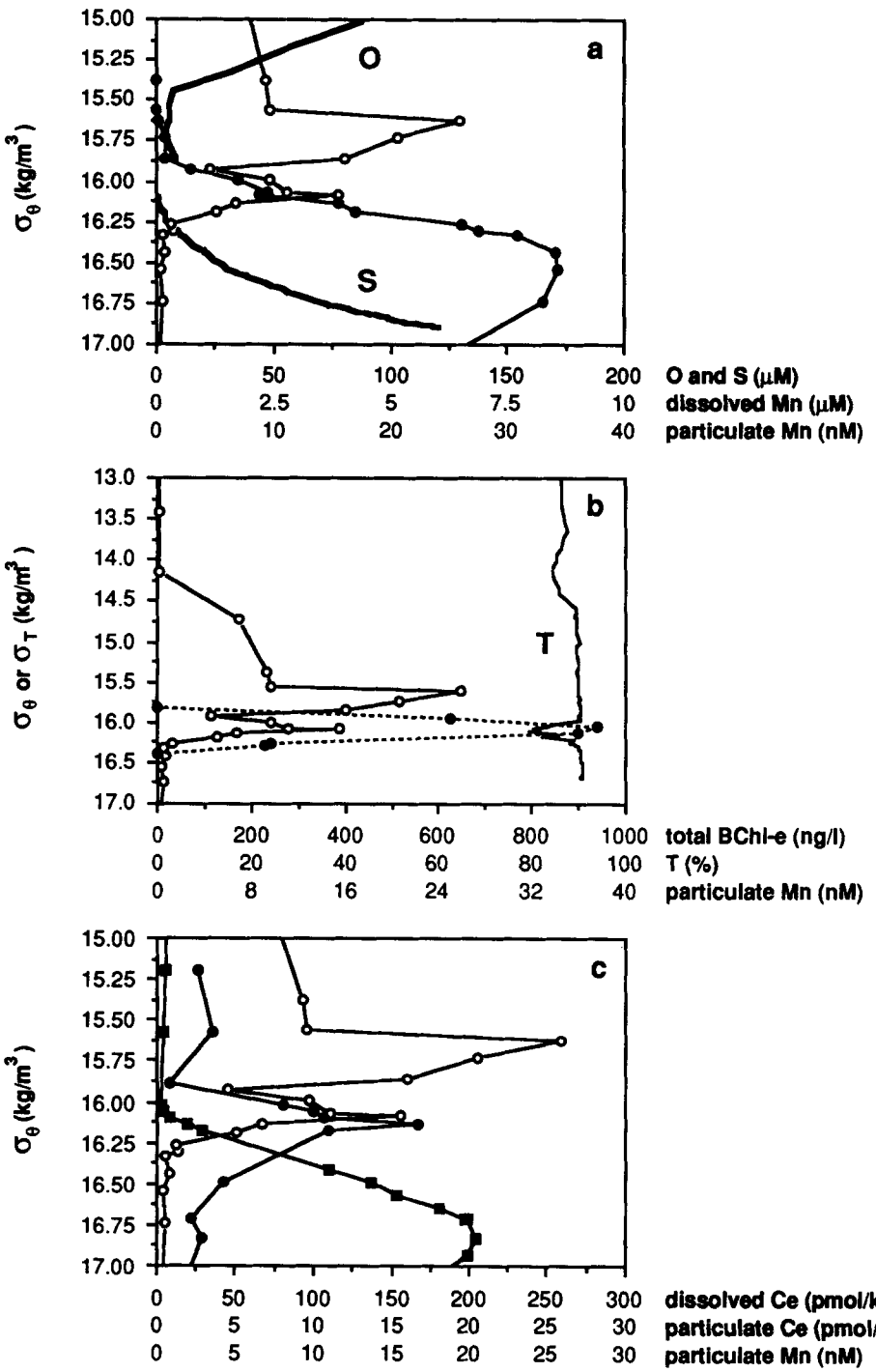
In an attempt to further elucidate the mechanism behind REE cycling in the suboxic zone of the Black Sea, we performed four experiments at station BS5-2 that simulate the mixing of well-oxygenated, particle-rich waters with anoxic, sulfidic waters rich in dissolved REE. Although we realize that such mixing may not actually occur in the Black Sea and that our experiments more closely simulate processes that take place near hydrothermal vents (Olivarez and Owen, 1989) or in anoxic basins where the oxic–anoxic interface is strongly vertically compressed, for example the Cariaco Trench (De Baar et al., 1988), we feel that certain factors make our experiments pertain more directly to the situation in the suboxic zone of the Black Sea, such as the composition of the particulate matter and the presence of certain unique species of bacteria. The broad suboxic zone close to the surface allowed pure end-members to be easily obtained, thus making the Black Sea particularly suitable for our experiments.

Special emphasis was given to the kinetics of REE scavenging, i.e. to the progression of the reactions with time and to reaction rates. In two of the experiments the role of bacteria and particulate matter was determined respectively. By comparing the results for Ce (a redox reactive REE) and Nd (a non-redox reactive REE) the importance of oxidative Ce scavenging was assessed. As yet, very few studies have specifically addressed the kinetics of (oxidative) Ce scavenging. Apart from an early study by Carpenter and Grant (1967), two excellent studies were recently published by Moffett (1990, 1993), who used radiotracers to monitor the scavenging of Ce in coastal seawater from Vineyard Sound and Chesapeake Bay and in water from the Sargasso Sea. He observed that rapid Ce adsorption plays an important role in Ce uptake and that Ce oxidation, even when entirely microbially mediated as it invariably seems to be in natural waters, is a relatively slow process that significantly contributes to Ce uptake only in regions of long particle residence time (low particle flux) or high bacterial abundance. The results of our study are in general agreement with these findings.

2. Sampling and analysis

Mixing experiments were performed on four consecutive days (23–26 July 1988) at station BS5-2 (43°06′N, 34°00′E) in the centre of the Black Sea (Fig. 1). Each morning two seawater samples, which we will refer to as "end-members", were freshly collected in 30 l GoFlo bottles mounted on a CTD/Rosette frame. One end-member was collected at a depth of about 300 dbar ($\sigma_\theta = 16.82\,kg/m^3$), where the dissolved REE reach their maximum concentrations and the concentration of sulfide is approximately 100 μM (Schijf et al., 1991; Schijf, 1992). The other end-member was collected at the depth of the particle maximum (PM), as defined by a distinct minimum in the light transmission profile (Fig. 2b). The center of this minimum was not well-defined, hence the potential density of the PM end-members varied between $\sigma_\theta = 16.05$ and $16.25\,kg/m^3$ (see also below). No oxygen was present within this depth range, yet the deeper PM end-members may have contained traces of sulfide.

As soon as the CTD/Rosette frame was on deck, aliquots of both end-members were filtered through 0.2 μm polycarbonate membrane filters (Nuclepore, ϕ142 mm). Filtered 300 dbar end-member and filtered and unfiltered PM end-member were collected for REE analysis in hot-acid-cleaned 60 ml LDPE narrow-mouth bottles and acidified to pH 2 with triple quartz-distilled 6.5 N HCl. In addition, either filtered or unfiltered 300 dbar end-member was collected in a hot-acid-cleaned 5 l LDPE narrow-mouth bottle. The mixing experiments were performed in the same 31 reaction vessel that was used to study sulfide oxidation in the Black Sea (Millero, 1991) and that was described in detail by Millero et al. (1987). The reaction vessel was first rinsed and then filled with either filtered or unfiltered PM end member, which was subsequently left to equilibrate with the atmosphere at a temperature of 25°C for at least


a
O
S
σ_θ (kg/m^3)
15.00
15.25
15.50
15.75
16.00
16.25
16.50
16.75
17.00
0 50 100 150 200 O and S (μM)
0 2.5 5 7.5 10 dissolved Mn (μM)
0 10 20 30 40 particulate Mn (nM)
b
T
σ_θ or σ_T (kg/m^3)
13.0
13.5
14.0
14.5
15.0
15.5
16.0
16.5
17.0
0 200 400 600 800 1000 total BChl-e (ng/l)
0 20 40 60 80 100 T (%)
0 8 16 24 32 40 particulate Mn (nM)
c
σ_θ (kg/m^3)
15.00
15.25
15.50
15.75
16.00
16.25
16.50
16.75
17.00
0 50 100 150 200 250 300 dissolved Ce (pmol/kg)
0 5 10 15 20 25 30 particulate Ce (pmol/kg)
0 5 10 15 20 25 30 particulate Mn (nM)

1 h. The 5 l LDPE narrow-mouth bottle with the 300 dbar end-member was closed and placed in a waterbath at 25°C for the same period of time. At $t = 0$ one part of 300 dbar end-member was mixed in the reaction vessel with three parts of PM end-member and the reaction vessel was closed. Concentrations of oxygen and sulfide were not determined, but Millero (1991), who performed identical experiments during Leg 5 of the 1988 Black Sea Expedition at the same station, reported average oxygen and sulfide concentrations at $t = 0$ of about 165 μM and 25 μM, respectively. Throughout each mixing experiment a constant temperature of 25°C was maintained inside the reaction vessel and the mixture was continuously stirred with a magnetic stirring bar. Subsamples were collected through 0.2 μm polycarbonate membrane filters (Millipore Swinnex-25 disc filter holder) into hot-acid-cleaned 60 ml LDPE narrow-mouth bottles and acidified to pH 2 with triple quartz-distilled 6.5 N HCl. Roughly, subsamples were taken every 15–30 min for a period of 1–2 h, then every hour for a period of 2–3 h and finally every 2–3 h until the end of the day. One final subsample was taken the next morning.

Mn concentrations were determined by GFAAS after ten-fold dilution of 1 ml of sample with Milli-Q water, using standard calibration curves in triple quartz-distilled 0.1 N HNO_3. Because of its low Mn concentration the filtered PM end-member that was collected on 23 July 1988 (experiment 4) was injected without dilution and no correction was made for possible matrix effects. Within the precision of the analyses (~5%) no variation in the Mn concentration with time could be resolved for any of the mixing experiments. Therefore, only end-member Mn concentrations, which are used for comparison with end-member REE concentrations, are presented here (Table 1).

The remainder of each sample was overspiked about ten-fold by adding 0.03–0.05 g of a spike solution containing all REE. Overspiking, which is a potential source of error during IDMS analysis of the REE, was necessary to avoid the much larger weighing errors that would accompany addition of the appropriate amount of spike solution. The samples were left to equilibrate with the spike solution for one week.

Table 1
Concentrations of Mn, Ce and Nd in filtered (f) and unfiltered (u) end-members, which were freshly collected shortly before each mixing experiment. End-members that were actually used in the experiments are indicated with an asterisk (*). The unfiltered 300 dbar end-member that was used in experiment 1 was not analyzed separately

End-member	Mn (μmol/kg)	Ce (pmol/kg)	Nd (pmol/kg)
Experiment 1			
PM f	3.03	25.52	21.77
PM u^*	3.81	33.28	20.57
300 dbar f	8.04	202.33	79.88
Experiment 2			
PM f	6.36	45.25	23.99
PM u^*	6.37	51.00	25.75
300 dbar f^*	6.86	207.37	81.15
Experiment 3			
PM f	2.39	17.23	14.17
PM u^*	2.87	22.28	15.87
300 dbar f^*	7.07	205.02	80.53
Experiment 4			
PM f^*	0.025	5.03	7.60
300 dbar f^*	6.82	203.74	80.15

PM = particle maximum.

The REE were pre-concentrated with Chelex 100 resin using the method of De Baar et al. (1988), modified after Schijf (1992). After pre-concentration, the REE were separated from remaining seasalt cations and Ba and divided into two fractions (one containing La and some of the Ce and one containing Ce–Lu) with AG 50W-X8 cation-exchange resin, using the method of De Baar et al. (1988), modified after Schijf (1992). The small subsample size (~50 ml) allowed only Ce and Nd to be analyzed with acceptable

Fig. 2. (a) Concentrations of dissolved oxygen (O) and sulfide (S), dissolved Mn (closed symbols) and particulate Mn (open symbols) at station BS5-2, as a function of σ_θ. The watercolumn is suboxic approximately between 75 and 110 dbar ($\sigma_\theta \approx 15.5$–$16.1$ kg/m^3). (b) Light transmission (T) and concentrations of particulate Mn (open symbols) at station BS5-2 and concentrations of total bacteriochlorophyll-e (closed symbols) at station BS2-2 (42°50′N, 32°00′E; Repeta et al., 1989). Light transmission is shown as a function of σ_T. (c) Concentrations of particulate Mn (open circles) and Ce (closed circles) and dissolved Ce (closed squares) at station BS5-2. Vertical distributions of Nd are similar to those of Ce.

Table 2
Concentrations of dissolved Ce and Nd as a function of time. Each subsample was collected the indicated number of minutes after the mixing of the two end-members ($t = 0$). Concentrations in parentheses exceed those of the 300 dbar end-member, probably as a result of contamination. The corresponding subsamples were not included in Figs. 4, 5 and 6

t (min)	Ce (pmol/kg)	Nd (pmol/kg)
Experiment 1, 25 July 1988, PM *u* + 300 dbar *u*		
10	139.10	59.58
25	135.77	55.25
42	102.12	45.69
60	91.63	42.50
92	93.06	44.50
120	83.38	37.44
182	89.60	40.79
299	79.02	38.18
449	–	–
612	79.05	37.74
1294	106.42	49.92
Experiment 2, 24 July 1988, PM *u* + 300 dbar *f*		
5	(682.17)	(283.59)
18	139.06	68.35
35	115.53	53.37
51	117.91	52.58
72	86.49	41.36
96	92.23	45.73
130	70.67	35.71
191	–	–
248	85.01	40.60
307	–	–
429	93.72	44.17
552	102.31	44.52
1193	144.70	62.37
Experiment 3, 26 July 1988, PM *u* + 300 dbar *f* + 20 ml formaldehyde		
18	(462.57)	(181.81)
55	119.85	53.77
84	102.26	48.14
115	87.26	36.61
143	82.92	39.87
205	75.97	–
319	86.51	41.69
503	68.83	38.02
630	95.32	47.46
1191	83.60	45.52
Experiment 4, 23 July 1988, PM *f* + 300 dbar *f*		
17	93.00	41.22
78	87.10	44.08
136	110.44	64.15
196	126.34	60.85
373	(214.10)	(86.66)
560	86.46	46.97
740	(224.85)	(89.70)
1280	116.15	43.50

PM = particle maximum, u = unfiltered, f = filtered.

accuracy and precision. Therefore, only the Ce–Lu fraction was kept for analysis, the La–Ce fraction was discarded. All reagents that were used for preconcentration and separation of the REE had first been cleaned either by multiple subboiling quartz-distillation or by subboiling quartz-distillation followed by further cleaning over a Chelex column.

Ce and Nd concentrations were determined by IDMS on a Finnigan MAT 261 thermal ionization mass spectrometer, using double Re-filament arrays. Errors in the concentrations were estimated by projecting the statistical errors in the isotopic ratios (1σ) on the calculated REE concentrations via the isotope dilution curve. They were generally $< 2\%$ for Ce and $< 5\%$ for Nd, somewhat larger than what is found in general for IDMS analysis of the REE in 21 seawater samples (Schijf, 1992). This is probably due to poor signal stability as a result of the small sample size or to the overspiking of the samples.

The small sample size also made the blank problem, usually negligible when 21 seawater samples are analyzed, a matter of some concern. The average of two procedural blanks was determined to be 0.308 pmol for Ce and 0.071 pmol for Nd. For a 50 ml sample this amounts to 6.2 pmol/kg for Ce and 1.4 pmol/kg for Nd, which is about 9 and 4% of the lowest Ce and Nd concentrations in Table 2, respectively. The determination of procedural blanks by IDMS suffers from low accuracy and precision and is therefore very irreproducible (Schijf, 1992). Consequently, although the average blanks are not negligible, they may not be representative of the actual procedural blank. Moreover, the discussion of the results will focus on reaction rates and since these are not significantly affected by correcting for the average blanks, such a correction was not performed.

3. Results

Ce and Nd end-member concentrations are presented in Table 1. Ce and Nd concentrations of the filtered 300 dbar end-members each show a total variation of only 2%, which is within the precision of the analyses. Ce and Nd concentrations of the filtered PM end-members show much larger variations, yet differences between Ce and Nd concentrations of unfiltered and filtered PM end-members, which tentatively represent particulate Ce and Nd concentrations, are always about 6 and 1.7 pmol/kg, respectively, except for experiment 1 where the Nd concentration of the unfiltered is somewhat lower than that of the filtered PM end-member. Latter numbers are of the same order as the particulate Ce and Nd concentrations that Schijf (1992) observed near the depth of the particle maximum (Fig. 2c).

While occupying station BS5-2 for more than one week, significant variability in the width and intensity of the light transmission minimum was observed, most likely due to the fact that station BS5-2 was located at the boundary between the two main Black Sea gyres. The light transmission minimum and hence the particle maximum was found to span the depth range 105–135 dbar (σ_θ = 16.05–16.25 kg/m^3), where the profiles of dissolved REE, Mn and Fe have strong concentration gradients, and within this depth range the light transmission profile often showed multiple minima, so that the center of the particle maximum was not well-defined. With the intention to always obtain the maximum amount of particulate matter, the PM end-members were actually collected at four different depths. These depth variations caused the variations in the Ce and Nd, and in the Mn (and probably Fe) concentrations of the filtered PM end-members (Table 1). The latter two are important, since they in turn may have caused variations in the amount of Mn and Fe oxides at $t = 0$, which was found to complicate the interpretation of the results. The variations in the Ce and Nd concentrations of the filtered PM end-members seem to have had little effect on the outcome of the experiments.

As shown in Fig. 3, the Ce and Mn concentrations of the filtered PM end-members (Table 1)

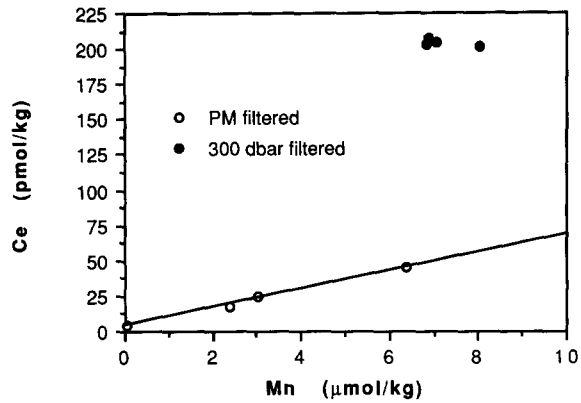


Fig. 3. Relationship between the Mn and Ce concentrations of the filtered PM and 300 dbar end-members.

are positively correlated. Between 105 and 135 dbar dissolved Ce and Mn concentrations increased nearly linearly with depth (German et al., 1991; Schijf et al., 1991). From the dissolved Ce and Mn gradients a linear relation between dissolved Ce and Mn concentrations could be derived that closely matched the fitted line in Fig. 3 (not shown). The same was found to hold for Nd and Mn. With increasing depth below 180 dbar dissolved Ce concentrations continued to increase, whereas dissolved Mn concentrations decreased again. This causes the linear relation to break down, which is why the filtered 300 dbar end-members form a separate cluster in Fig. 3. The above confirms that the variations in the Ce, Nd and Mn concentrations of the filtered PM end-members are due to depth variations and not to precipitation/adsorption processes or contamination.

Ce and Nd concentrations of the subsamples are presented in Table 2 as a function of time, which is expressed as the number of minutes after the mixing of the end-members ($t = 0$). Concentrations in parentheses exceed those of the filtered 300 dbar end-member. The corresponding subsamples were regarded as contaminated and not included in any of the figures.

In experiment 1, neither of the two end-members was filtered prior to mixing. Ce and Nd concentrations decreased rapidly until a minimum was reached after about 150 min (Table 2). Concentrations subsequently increased again at a much lower rate, a trend that still seemed to continue at

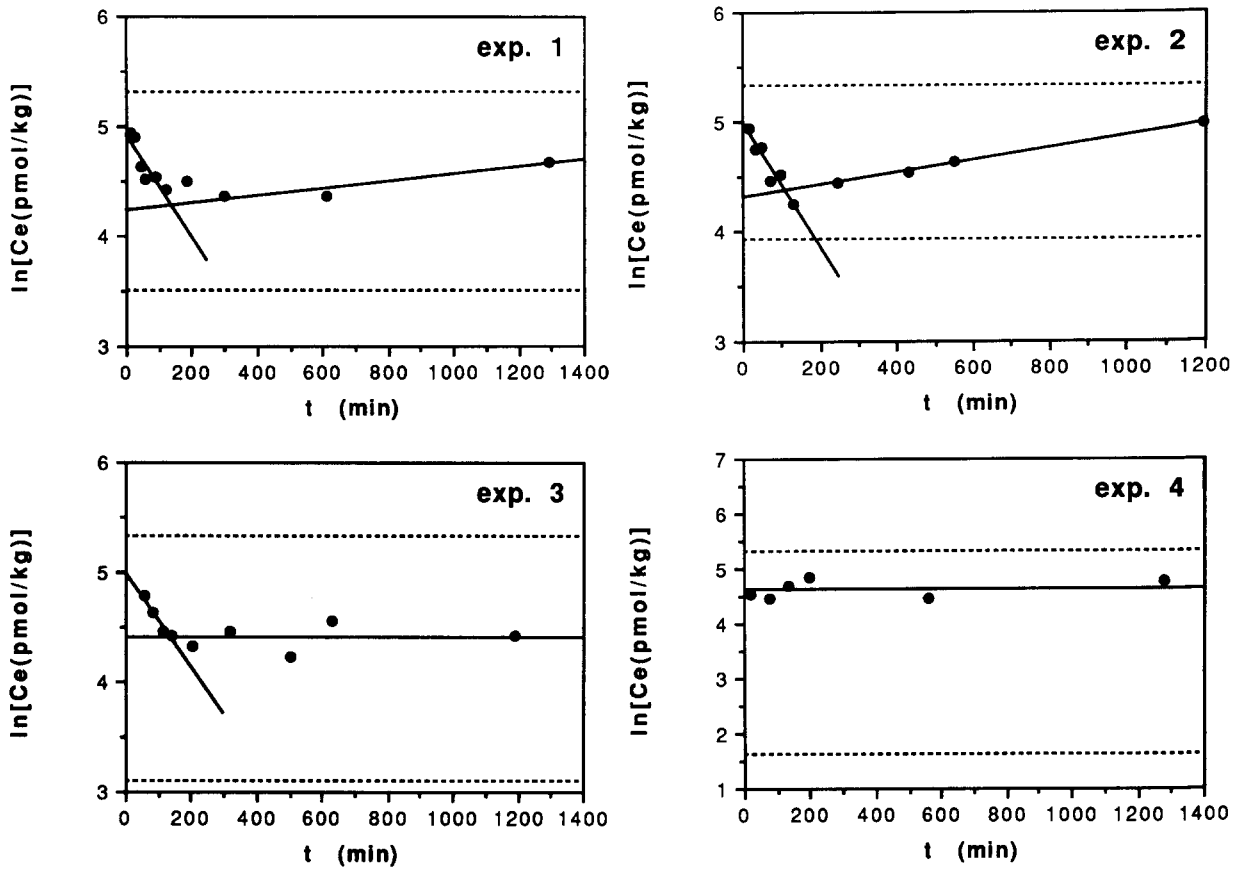


Fig. 4. The natural logarithm of Ce concentrations as a function of time, expressed as the number of minutes after the mixing of the two end-members ($t = 0$). End-member concentrations are indicated by dashed lines. Solid lines are fits to the data in the time intervals $0 < t < 150$ and $t > 150$, except for horizontal lines (see text).

the end of the experiment ($t = 1300$). In experiment 2, the 300 dbar end-member was filtered prior to mixing. Ce and Nd concentrations decreased rapidly during the first 150 min and then slowly increased again throughout the rest of the experiment, very similar to what was observed in experiment 1 (Table 2). The initial removal and subsequent release of Ce and Nd will hereafter be referred to as "reaction 1" and "reaction 2", respectively.

In Figs. 4 and 5 the natural logarithm of dissolved Ce and Nd concentrations is shown as a function of time. It must be noted that we have chosen this representation of the data merely for convenience and that we do not wish it to imply any specific type of process. It appears then that data in the time intervals $0 < t < 150$ and $t > 150$ obey pseudo first-order kinetics, as follows:

$$[M] = [M]_T \exp(kt) \tag{1a}$$

or, written differently:

$$[M]/[M]_T = \exp(kt) \tag{1b}$$

where $[M]$ is the dissolved Ce or Nd concentration, $[M]_T$ is the dissolved Ce or Nd concentration at $t = T$, and the pseudo first-order rate constants k are $-k_1'$ and k_2' for reactions 1 and 2, respectively. The latter were determined from linear fits to the data in plots of $\ln[M]$ vs. t, as shown in Figs. 4 and 5. Curves (1a) were fitted to data in the intervals $0 < t < 150$ and $t > 150$ to determine $-k_1'$ and k_2' respectively. The results are listed in Table 3. The cutoff at $t = 150$ is arbitrary and based solely on visual inspection of the data.

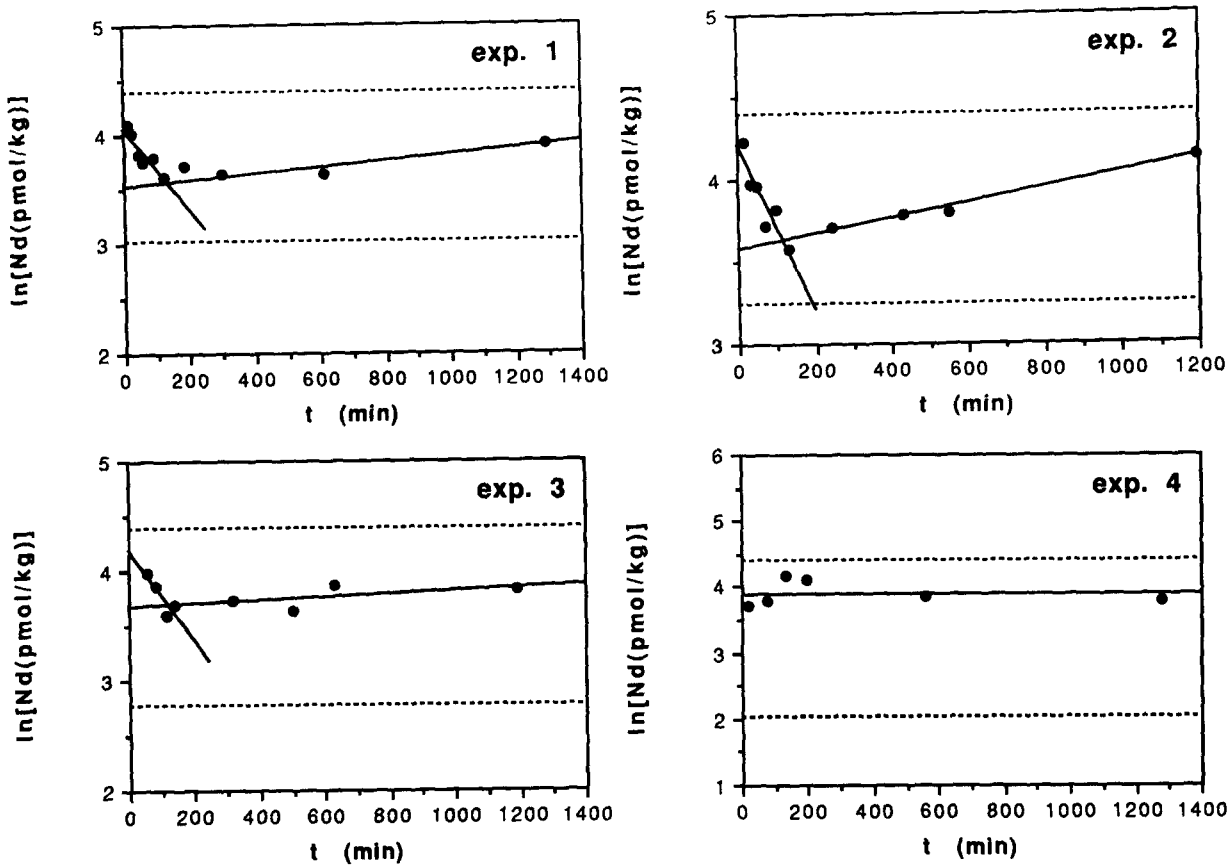


Fig. 5. The natural logarithm of Nd concentrations as a function of time. See also Fig. 4.

The $t = 182$ subsample in experiment 1 was considered an outlier and not used in the determination of the k_2'.

In order to determine whether the removal and/or the release of Ce and Nd were in any way microbially mediated, experiment 2 was repeated in experiment 3 with addition at $t = 0$ of 20 ml of formaldehyde (final concentration 0.7%), which is an inhibitor of microbial activity. Ce and Nd concentrations decreased during the first 150 min as before (Table 2). Nd then increased again very slowly throughout the rest of the experiment. On the other hand, Ce concentrations were found to be invariant with time for $t > 150$. The pseudo first-order rate constant k_2' for Ce was therefore assumed equal to zero. The horizontal line in Fig. 4 represents the mean of the natural logarithm of Ce concentrations in the time interval $t > 150$.

In order to determine the role of particulate matter, both end-members were filtered prior to mixing in experiment 4. Ce and Nd concentrations were found to be invariant with time throughout the experiment. It was therefore assumed that $k_1' = k_2' = 0$ for Ce as well as for Nd. The horizontal lines in Figs. 4 and 5 represent the mean of the natural logarithm of Ce and Nd concentrations in the time interval $t > 0$, respectively.

4. Discussion

As shown in Table 1, the PM end-members contained large amounts of dissolved Mn (and probably Fe). During equilibration of the PM end-member with the atmosphere some of this Mn and Fe was most likely oxidized to insoluble Mn and Fe oxides. Mn oxidation, even when

Table 3
Pseudo first-order rate constants (min^{-1}) for the initial removal (k'_1) and subsequent release (k'_2) of Ce and Nd. k'_1 and k'_2 were determined from linear fits to the data for $0 < t < 150$ and $t > 150$, respectively. Numbers r in parentheses are linear correlation coefficients. Rate constants equal to zero correspond to the horizontal lines in Figs. 4 and 5, which are not fits to the data. k'_{Ce} and k'_{Nd} were determined as described in the text

	Ce	Nd
Experiment 1		
k'_1 ($n = 6$)	$4.65 \cdot 10^{-3}$ ($r = 0.90$)	$3.75 \cdot 10^{-3}$ ($r = 0.91$)
k'_2 ($n = 3$, $t = 182$ rejected)	$3.21 \cdot 10^{-4}$ ($r = 0.95$)	$2.92 \cdot 10^{-4}$ ($r = 0.94$)
Experiment 2		
k'_1 ($n = 6$)	$5.68 \cdot 10^{-3}$ ($r = 0.95$)	$5.04 \cdot 10^{-3}$ ($r = 0.92$)
k'_2 ($n = 4$)	$5.63 \cdot 10^{-4}$ ($r = 1.00$)	$4.58 \cdot 10^{-4}$ ($r = 0.99$)
Experiment 3		
k'_1 ($n = 4$)	$4.29 \cdot 10^{-3}$ ($r = 0.98$)	$4.01 \cdot 10^{-3}$ ($r = 0.87$)
k'_2 ($n = 5$, $t = 143$ included)	0	$1.39 \cdot 10^{-4}$ ($r = 0.60$)
Experiment 4		
k'_1	0	0
k'_2	0	0
Experiments 1 and 2 combined		
k'_{Ce} ($n = 12$)	$5.26 \cdot 10^{-3}$ ($r = 0.92$)	
k'_{Nd} ($n = 12$)		$4.51 \cdot 10^{-3}$ ($r = 0.89$)

microbially mediated, is known to be a relatively slow process (Tebo et al., 1984). Tebo (1991) showed that the potential Mn(II) removal rate, i.e. the Mn(II) removal rate under fully oxygenated conditions, is only about 0.5%/h at the depth of the particle maximum. Fe oxidation on the other hand proceeds rapidly under fully oxygenated conditions (Roekens and Van Grieken, 1983). The PM end-member of experiment 2, which contained 6.4 μM dissolved Mn (Table 1) and probably about 80 nM dissolved Fe (Lewis and Landing, 1991), is expected to have formed no more than 30 nM Mn oxides and 80 nM Fe oxides during the 1 h equilibration, while Mn and Fe oxides already present before the equilibration may have added another 10 nM to each. This means that no more than 10 nM Mn oxides and about 20 nM Fe oxides were present at $t = 0$. The PM end-members of the other experiments contained less dissolved Mn and Fe so that proportionally less Mn and Fe oxides may have been present at $t = 0$. Unfortunately, the small subsample size did not allow particulate Mn and Fe concentrations to be measured at $t = 0$ or at any other time during the experiments.

4.1 Experiments 1 and 2

Experiment 2 is identical to experiment 1, except for the filtration of the 300 dbar end member, which should not have had a significant effect, since it contained much less particulate matter and particulate Mn, Fe and REE than the PM end-member (Fig. 2; Lewis and Landing, 1991). The results of experiments 1 and 2 are indeed very similar, as can be seen from Figs. 4 and 5, and will be discussed together in this section.

Since Nd is not a redox reactive element, its removal during reaction 1 in experiments 1 and 2 was probably caused by adsorption onto particulate matter. The Mn and Fe oxides that formed during equilibration of the PM end-member with the atmosphere are known to be excellent scavengers of the REE (Wang et al., 1983; Olivarez and Owen, 1989; Byrne and Kim, 1990) and are therefore prime candidates for the removal of Nd during reaction 1. On the basis of the available data it is not possible to determine whether Mn oxides, Fe oxides, or both were responsible, yet, as suggested by their presumably higher concentration at $t = 0$ and their increasing importance after $t = 0$, which

is discussed below, Fe oxides may have played a somewhat larger role.

In addition to removal by adsorption onto particulate matter, the redox reactive element Ce may have been removed during reaction 1 by its oxidation to insoluble Ce oxides. The pseudo first-order rate constants k'_1 for Ce in experiments 1 and 2 are $4.65 \cdot 10^{-3}$/min and $5.68 \cdot 10^{-3}$/min, or 28%/h and 35%/h, respectively (Table 3). Moffett (1990, 1993) found that specific Ce oxidation rates in the Sargasso Sea, Vineyard Sound and Chesapeake Bay, while spanning three orders of magnitude, were always just slightly lower than, or at most equal to, corresponding specific Mn oxidation rates. The specific Ce oxidation rate at the depth of the particle maximum is therefore expected not to be larger than the potential Mn(II) removal rate at that depth, 0.5%/h (Tebo, 1991). Ce adsorption rates were not explicitly reported for Moffett's studies, but Moffett (1990) did state that "Ce(III) uptake occurs on a shorter timescale than Ce(III) oxidation". Ce oxidation, notwithstanding its lower rate, can be important on longer timescales (Moffett, 1990), yet the limited timescale of experiments 1 and 2 and the very high k'_1 strongly suggest that adsorption onto Mn and/or Fe oxides is the major mechanism for Ce removal during reaction 1.

Both in experiment 1 and 2 the pseudo first-order rate constants k'_1 are higher for Ce than for Nd, which may be due to Ce oxidation, or to a different degree of complexation for Ce and Nd, causing Ce to be removed more effectively than Nd (Elderfield, 1988; Byrne and Kim, 1990). Also, both for Ce and Nd the k'_1 are higher in experiment 2 than in experiment 1, which may be due to the higher concentration of Mn (and probably also of Fe) in the PM end-member of experiment 2, possibly leading to a larger amount of Mn and Fe oxides at $t = 0$ and hence to enhanced adsorption of Ce and Nd. However, considering that the precision with which the k'_1 could be determined is no more than about 20% (1σ) as a result of the limited amount of data, the aforementioned differences may be insignificant.

In order to obtain a more precise determination of the pseudo first-order rate constants k'_1 for Ce and Nd, data from experiments 1 and 2 in the time interval $0 < t < 150$ were combined. All Ce and Nd concentrations were normalized respectively to $[Ce]_0$ and $[Nd]_0$, the Ce and Nd concentrations at $t = 0$, which were determined from the fits in Figs. 4 and 5. As before, the data obey pseudo first-order kinetics. Pseudo first-order rate constants $-k'_{Ce}$ and $-k'_{Nd}$ were determined from linear fits to the data in plots of $\ln([M]/[M]_0)$ vs. t, as shown in Fig. 6. Curves (1b) were fitted to the data for Ce and Nd to determine $-k'_{Ce}$ and $-k'_{Nd}$ respectively. The results are listed in Table 3.

Despite the improved precision of about 15% (1σ), the difference between k'_{Ce} and k'_{Nd} may still be insignificant, again suggesting that Ce removal during reaction 1 is largely caused by adsorption onto Mn and/or Fe oxides and that Ce oxidation plays only a minor role. It must be noted that the

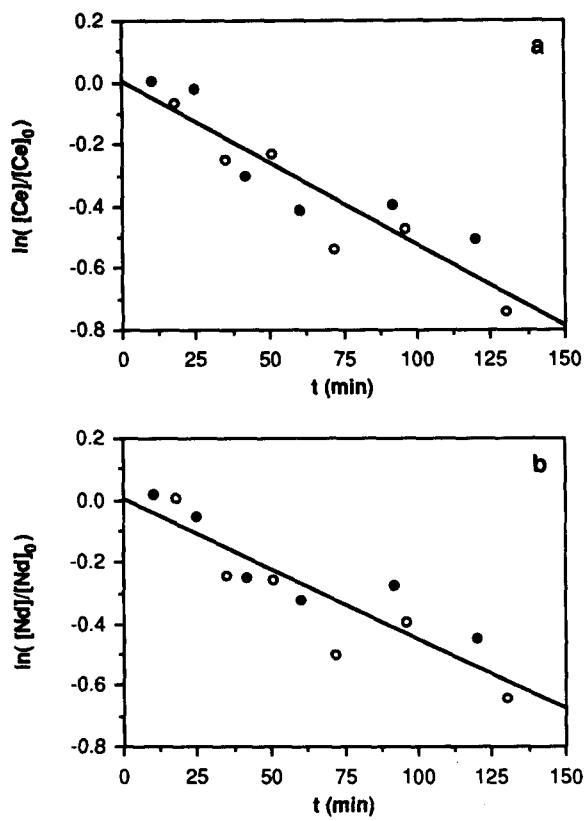


Fig. 6. The natural logarithm of (a) Ce and (b) Nd concentrations, normalized to Ce and Nd concentrations at $t = 0$, as a function of time in the time interval $0 < t < 150$. Data from experiments 1 (closed symbols) and 2 (open symbols) combined. Solid lines are fits to the data.

relative contribution to Ce uptake of oxidation on the one hand and adsorption on the other hand strongly depends on factors such as particle residence time and bacterial abundance and can vary substantially with place and time (Moffett, 1990, 1993). For instance, De Baar et al. (1988), who derived relative REE turnover rates from dissolved REE gradients at the oxic–anoxic interface of the Cariaco Trench, found the ratio of Ce and Nd turnover rates to be 2.7 : 1, which is clearly different from the ratio 1.2 : 1 of k'_{Ce} and k'_{Nd} (Table 3), and attributed the excess cycling of Ce to its unique redox chemistry.

The release of Ce and Nd after 2.5 h is most intriguing. It is about one order of magnitude slower than the initial removal of Ce and Nd (Table 3). Like the k'_1, the pseudo first-order rate constants k'_2 are larger for Ce than for Nd and larger in experiment 2 than in experiment 1. Although the standard deviations of the k'_2 in experiment 1 are large because of the limited number of measurements for $t > 150$ ($n = 3$, $t = 182$ was rejected), these differences seem to be more significant than for the k'_1.

Release after initial removal was also reported for Mn by Tebo (1991), who studied Mn oxidation during Leg 3 of the 1988 Black Sea Expedition. At station BS3-6 (the same location as station BS5-2) at depths of 72 and 76 m ($\sigma_\theta = 15.52$ and 15.65 kg/m^3, respectively) he observed rapid removal of a ^{54}Mn tracer in the absence of oxygen, followed after 2.5 h by slower release back into solution. He attributed the removal to exchange of ^{54}Mn(II) with Mn(II) bound to surfaces and the subsequent release to the dissolution of particulate matter, possibly manganate(III, IV) minerals.

It is not likely that either of the end-members in experiments 1 and 2 contained any soluble REE minerals, nor that such minerals were formed before or during the experiments, so the explanation of Tebo (1991) is not valid for Ce and Nd. Since Nd is not a redox reactive element its release during reaction 2 can only have been caused by dissolution of the Mn and/or Fe oxides onto which it was adsorbed. At $t = 0$ sulfide was introduced with the 300 dbar end-member, which contained about 100 μM, to a final concentration of about 25 μM. In identical experiments Millero (1991) observed that, upon mixing of the end-members, this sulfide was consumed at a constant rate due to oxidation. Luther et al. (1991) and Millero (1991) independently suggested that, in the Black Sea, sulfide is oxidized by Mn and Fe oxides. Conversely, the dissolution of Mn and Fe oxides in our experiments may have been due to reduction by sulfide.

Alternatively, throughout the suboxic layer Nealson et al. (1991) found several species of bacteria capable of reducing both Mn and Fe oxides. Especially abundant at the depth of the particle maximum was the species *Shewanella putrefaciens*, which displays a remarkable respiratory versatility, i.e. it can use a variety of electron acceptors for the oxidation of organic matter, including oxygen, nitrate, nitrite, Mn oxides and Fe oxides. These bacteria may well have been present in the (unfiltered) PM end-member.

Whether caused by sulfide or by bacteria, reduction of Mn and Fe most likely commenced directly upon mixing and if bacteria were involved even before mixing. Apparently this did not initially interfere with the adsorption of Ce and Nd, for which there are several possible reasons. First, the rate of Ce and Nd adsorption may have been so much higher than that of Mn and Fe reduction, that any Ce or Nd released by the dissolution of Mn and/or Fe oxides was immediately readsorbed, until 2.5 h after mixing the amount of Mn and/or Fe oxides became too small for the adsorption of Ce and Nd to continue. Further dissolution of Mn and/or Fe oxides then caused Ce and Nd to be released at a rate that was controlled by the rate of Mn or Fe reduction. Second, Fe oxides may have survived in the presence of sulfide for quite some time. Although both Mn oxides and Fe oxides are rapidly consumed in the presence of sulfide (Millero, 1991), the rate of Fe oxidation may have been high enough to compete with the dissolution of Fe oxides, as long as oxygen was present in the mixture. The rate of Mn oxidation on the other hand, would be too low to compete with the dissolution of Mn oxides, even in the presence of oxygen, causing Fe oxides to play an increasingly important role in the adsorption of Ce and Nd. Finally, substantial amounts of dissolved

Mn and Fe were introduced with the 300 dbar end-member at $t = 0$. Again, the high rate of Fe oxidation may have caused the dissolved Fe to oxidize even in the presence of sulfide, further enhancing the effective lifespan of Fe oxides.

If the reduction of Mn and Fe was microbially mediated, an alternative explanation for the change from removal to release presents itself. Possibly, microbially mediated Mn and Fe reduction was triggered 2.5 h after mixing by certain conditions that were brought about by reaction 1, for instance, before starting on the Mn and/or Fe oxides the bacteria may have preferred some other oxidant that became exhausted 2.5 h after mixing.

4.2 Experiment 3

In view of the possibility that the Mn (and Fe) concentrations of the PM end-member affected the rates of Ce and Nd removal during reaction 1, the results of experiment 3, which is really a repetition of experiment 2, are compared here with those of experiment 1, since the Mn concentration of the PM end-member was much higher in experiment 2 than in experiment 3 (Table 1). Formaldehyde was not added until $t = 0$ and therefore cannot have affected the formation of Mn and/or Fe oxides during equilibration of the PM end-member with the atmosphere.

The addition of formaldehyde had no effect on the pseudo first-order rate constants k_1' (Table 3), yet, as was argued before, the rate of Ce and Nd adsorption may have been so much higher than that of Mn and Fe reduction, that inhibition of the latter by formaldehyde probably would not initially affect the removal of Ce and Nd. Reaction 1 therefore yields no clues as to whether the reduction of Mn and Fe was microbially mediated or not. Being an abiotic process, a direct effect of formaldehyde on the adsorption of Ce and Nd onto Mn and/or Fe oxides is not to be expected.

The pseudo first-order rate constants k_2' (Table 3) show that the rate of Nd release was inhibited by about 50% in the presence of formaldehyde, while Ce release was completely eliminated ($k_2' = 0$), as indicated by the horizontal line in Fig. 4. Since the rate of Ce and Nd release during reaction 2 was controlled by the rate of Mn or Fe reduction, the inhibition of Ce and Nd release indicates that Mn and/or Fe reduction were inhibited and hence, at least for a major part, microbially mediated. It is not clear why the release of Ce was more strongly inhibited than that of Nd.

The action of the formaldehyde must be interpreted with some caution, because formaldehyde is known to affect the solution chemistry of Mn. Rosson et al. (1984) found that 2% formaldehyde causes 44% desorption of ^{54}Mn tracer from Mn oxide (δMnO_2) after 1 h and that 3.7% formaldehyde causes 7% dissolution of the same Mn oxide after 30 min. However, the effect of this during reaction 2 would be to enhance rather than inhibit the release of Ce and Nd and the conclusion that Mn and/or Fe reduction were microbially mediated therefore remains unchanged.

4.3 Experiment 4

In experiment 4 neither removal nor release of Ce and Nd was observed ($k_1' = k_2' = 0$), as signified by the horizontal lines in Figs. 4 and 5. The purpose of this experiment, in which both end-members were filtered prior to mixing, was to determine the role of particulate matter. Unfortunately, interpretation of the results is complicated by the low concentrations of dissolved Mn and Fe in the PM end-member, which are 25 nM (Table 1) and about 5 nM (Lewis and Landing, 1991), respectively, at least one order of magnitude lower than in any of the other experiments. Even if all this Mn and Fe were oxidized during equilibration with the atmosphere, the amount of Mn and Fe oxides at $t = 0$ may have been too low for adsorption of Ce and Nd to occur at any rate. It was suggested above that reaction 2 may have been triggered by certain conditions that were brought about by reaction 1. In that case, reaction 2 simply did not occur because these conditions failed to be created.

However, the actual concentrations of Mn and Fe oxides at $t = 0$ were probably still two orders of magnitude higher than the concentrations of dissolved Ce and Nd at $t = 0$. It could therefore be argued that reactions 1 and 2 would still have occurred as in experiments 1 and 2, had not both

end-members been filtered. Filtration of the PM end-member may have removed the Mn and Fe reducing bacteria that were presumably present in the other three experiments. This would strongly inhibit, if not eliminate, reaction 2, yet it would not affect reaction 1, the abiotic adsorption of Ce and Nd onto Mn and/or Fe oxides, unless the oxidation of Mn or Fe during equilibration with the atmosphere was microbially mediated or otherwise required the presence of particulate matter.

5. Conclusion

Upon mixing of anoxic Black Sea water from the depth of the dissolved REE maxima (300 dbar) with water from the depth of the particle maximum (PM) that had first been equilibrated with the atmosphere, dissolved Ce and Nd were removed from solution for approximately 2.5 h and subsequently released for at least 20 h. Both processes were found to obey pseudo first-order kinetics, while rates of release were about ten times lower than rates of the initial removal.

The initial removal of Ce and Nd was probably governed by adsorption onto fresh Mn and/or Fe oxides that formed during equilibration of the PM end-member with the atmosphere. Differences in removal rates between the various experiments seem to be related to the concentrations of dissolved Mn and Fe in the PM end-member (the experiment with the lowest concentrations showed no removal whatsoever). Apparently, the rates of Ce and Nd adsorption were determined by the amount of Mn and/or Fe oxides present at $t = 0$. Ce removal rates were almost two orders of magnitude higher than an estimate of the Ce oxidation rate at the depth of the particle maximum based on studies by Moffett (1990, 1993), and very similar to Nd removal rates, strongly suggesting that Ce oxidation contributed negligibly to the removal of Ce.

The release of Ce and Nd was most likely the result of reductive dissolution of the Mn and/or Fe oxides onto which they were adsorbed. Some abiotic reduction of Mn and Fe may have been caused by sulfide that was introduced with the 300 dbar end-member, yet the fact that the release of Ce and Nd was inhibited in the presence of formaldehyde indicates that it was largely mediated by Mn and Fe reducing bacteria that were introduced with the (unfiltered) PM end-member.

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